Catalytic transfer hydrogenation by a trivalent phosphorus compound: phosphorus-ligand cooperation pathway or P(III) /P(V) redox pathway?

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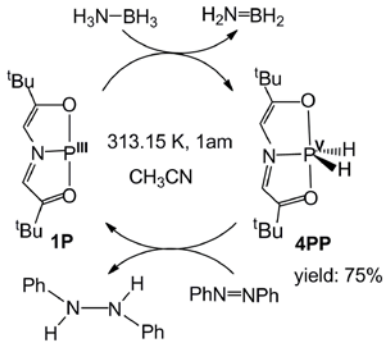
Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P^{III}/P^{V} Redox Pathway?**

*Guixiang Zeng,[1] Satoshi Maeda,[2] Tetsuya Taketsugu,[2] and Shigeyoshi Sakaki[1]**

Main-group element catalyst is a desirable alternative of transition metal catalyst, considering the use of abundant and less expensive element. But the examples are very limited. The catalytic cycle via redox process and E-ligand cooperation (E = main-group element), which are often found in catalytic cycle by transition metal catalyst, has not been reported yet. Here we theoretically investigated a catalytic hydrogenation of azobenzene with ammonia-borane by a trivalent phosphorus compound **1P**, which was experimentally proposed to occur through P^{III}/P^{V} redox processes via an unusual pentavalent dihydridophosphorane **4PP**. DFT and ONIOM(CCSD(T):MP2) calculations disclosed that this catalytic reaction occurs through P-O cooperation mechanism, which resembles well the metal-ligand cooperation mechanism by the transition metal catalyst. In this cycle, P,O-dihydrogenated trivalent phosphorus compound **4OP** is an active species, which is formed from **1P** through the dehydrogenation with ammonia-borane in a concerted manner. When azobenzene is absent, **4PP** is formed from **4OP** via a P^{III}/P^{V} redox process.

Main-group element compounds experience renaissance in the last decade for their excellent reactivities similar to those of transition metal complexes.[1] For instance, carbene and acetylene analogues of heavy main-group element compounds are reactive for H-H σ-bond activation via oxidative addition,[1a,2] and the Ge-H bond is reactive for the insertion reactions of C≡C triple and C=O double bonds.[1b,3] Though these are essentially the same as the elementary steps in the catalytic reactions by transition metal complexes, full catalytic cycles by main-group element compounds are limited[1c] except for the catalyses of several frustrated Lewis pairs.[4] As well-known, the catalytic cycles involving the metal-ligand cooperation and the redox process are often found in the chemistry of transition metal complexes, but they have not been reported for the main group element compound. Recently, Radosevich and his coworkers[5] reported an interesting catalytic reaction by a trivalent phosphorus compound 10-P-3 ADPO **1P** [6,7] and proposed a catalytic cycle via P^{III}/P^{V} redox processes; see Scheme 1. In this reaction, **1P** reacts with ammonia-borane to afford a pentavalent dihydridophosphorane, 10-P-5 ADPO·$(H)_2$ **4PP**, which catalyzes the hydrogenation of azobenzene to regenerate **1P**. However, the mechanistic details of these reactions and the role of **4PP** are still unclear. Such knowledge is necessary for further development of the chemistry of main group element compound.

In this work, we theoretically investigated all the reaction processes involved in Scheme 1. Geometry optimizations were carried out by the DFT[8] method with the B3PW91 functional,[9] where the AFIR method[10] was employed for optimizing several transition states. Electronic energies were calculated by the ONIOM(CCSD(T):MP2) method[11] in acetonitrile solution, where the CPCM model[12] was employed. Gaussian09[13] was used here; see Supporting Information (SI) for computational details. Throughout this paper, the discussion was presented based on the Gibbs energy changes relative to the sum of reactants (**1P** + ammonia-borane + azobenzene) unless otherwise noted. For convenience, the tri-ligated moiety coordinating with the phosphorus centre in **1P** is named an ONO ligand hereafter.



Scheme 1. Catalytic cycle of transfer hydrogenation by **1P**.

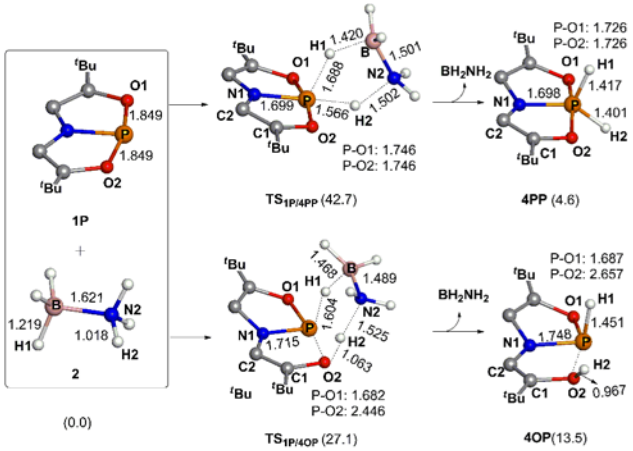


Figure 1. Geometry changes in the concerted oxidative addition and the P-O cooperation reaction pathways. Bond distances are in Å. In parentheses are the Gibbs energy changes (kcal/mol).

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For the dehydrogenation reaction of ammonia-borane, three kinds of reaction pathways are considered to be possible. One is the concerted oxidative addition, which occurs only on the phosphorus center through a transition state **TS$_{1P/4PP}$** to directly afford **4PP**; see Figure 1. It needs a large Gibbs activation energy ($\Delta G^{0\neq}$) of 42.7 kcal/mol, indicating that this reaction pathway is difficult; see Figure 2.

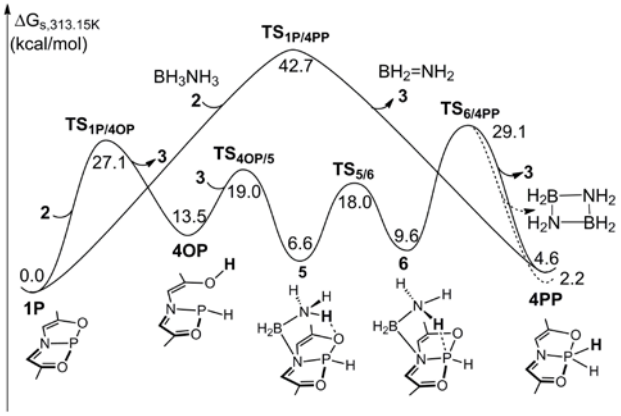


Figure 2. The Gibbs energy changes (in kcal/mol) in the dehydrogenation reaction of ammonia-borane by **1P**.

The second is the stepwise pathway, which occurs through the oxidative addition of the B-H or N-H σ-bond to the phosphorus centre followed by the β-hydrogen abstraction; see Figure S2 in SI. However, the Gibbs activation energy of the oxidative additions of the B-H and N-H σ-bonds are too large (70.0 and 60.4 kcal/mol, respectively) for the reaction to occur. This is contrast to the facile oxidative addition of the B-H σ-bond of ammonia-borane to the Ir(I) complex.[14]

The third is the P-ONO cooperation pathway, in which the phosphorus centre and one atom of the ONO ligand cooperatively react with ammonia-borane. The P-O cooperation pathway is the most favorable with a moderate $\Delta G^{0\neq}$ value of 27.1 kcal/mol, which is much smaller than those of the aforementioned pathways. In this step, an intermediate **4OP** is formed through a transition state **TS$_{1P/4OP}$** with the release of NH_2=BH_2. In **4OP**, the phosphorus centre has a usual three-coordinate structure, where the P-O2 bond is broken (2.657 Å). This P-O cooperative reaction is similar to the dehydrogenation of alcohols by transition-metal complexes with pincer ligand.[15] On the other hand, the P-C1, P-C2, and P-N1 cooperation pathways need much larger $\Delta G^{0\neq}$ values (56.1, 35.8, and 41.1 kcal/mol, respectively); see Figure S3 in SI. It should be noted that the phosphorus-ligand cooperation mechanism is firstly found here in the chemistry of main-group element compounds.

As shown in Figure 2, **4OP** is less stable than **4PP** by 8.9 kcal/mol. Also, **4PP** was experimentally isolated. Hence, we investigated the isomerization of **4OP** to **4PP**. In one-step intra-molecular pathway, the H2 atom directly migrates from the O2 atom to the phosphorus centre to yield **4PP**. However, this isomerization needs a large $\Delta G^{0\neq}$ value of 42.2 kcal/mol; see Figure S4. Several stepwise intra-molecular pathways, in which the H2 atom transfers from the O2 atom to the phosphorus centre via the C1, C2, or N1 atoms, also need large $\Delta G^{0\neq}$ values; see Figure S4.

Then, we investigated the NH_2=BH_2-assisted transformation of **4OP** to **4PP**, considering that one NH_2=BH_2 molecule was produced by the dehydrogenation reaction of ammonia-borane; see above. As shown in Figure 3, the BH_2 moiety of NH_2=BH_2 interacts with the N1 atom of **4OP** because the BH_2 moiety is a Lewis acid and the N1 moiety is a Lewis base; see Figure 3 for N1 etc. Simultaneously, the N2 atom of NH_2=BH_2 lifts the H2 atom from the O2 atom. This step occurs through a transition state **TS$_{4OP/5}$** to form a more stable intermediate **5**. In **5**, the NH_2 group converts to a NH_3 group and a B-N1 covalent bond is formed. At the same time, the B=N2 double bond changes to a B-N2 single bond; see Figure 3 for those bond distances. Interestingly, the P-N1 bond is kept and the phosphorus centre has a four-coordinate structure. After that, the BH_2-NH_3 moiety rotates around the B-N1 bond to bring the H2 atom toward the phosphorus atom through a transition state **TS$_{5/6}$** to afford an intermediate **6**. In **6**, the P-N1 bond is broken and the phosphorus centre returns to a usual sp^3-like structure with three coordinate bonds. Finally, the H2 atom moves to the phosphorus atom through a transition state **TS$_{6/4PP}$** to afford **4PP**. In this process, the P-N1 bond is formed again and the phosphorus centre changes from the

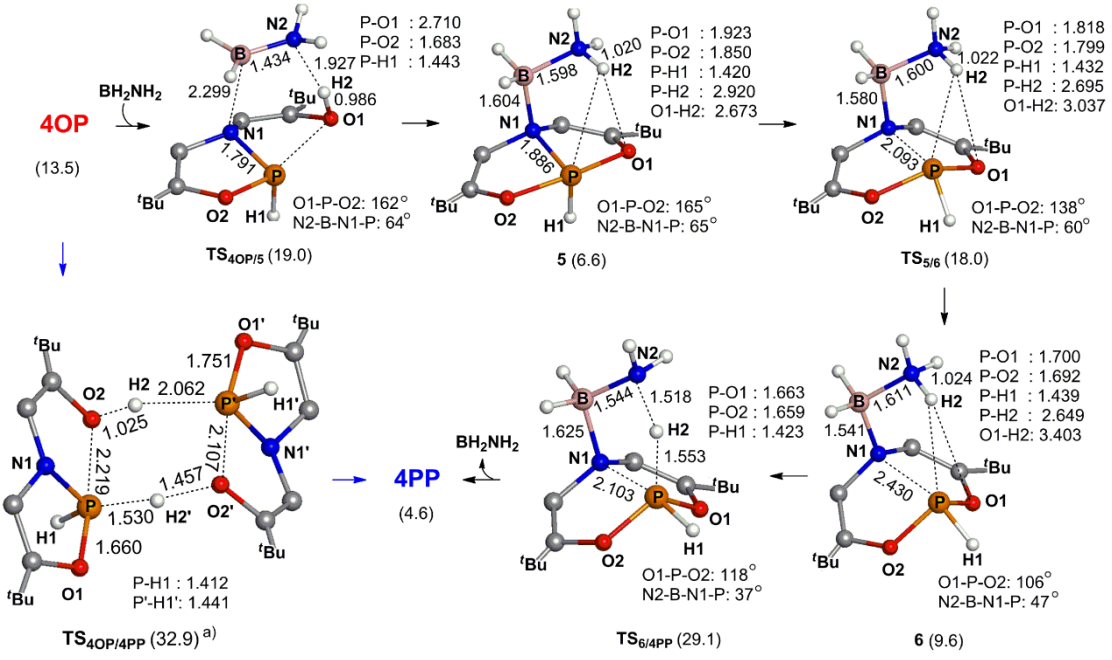


Figure 3. Geometry changes in the isomerization of **4OP** to **4PP**. Distances are in Å. a) The B3PW91-calculated value. The Gibbs activation energy is comparable with that of the NH_2=BH_2-assisted pathway.[16]

three-coordinate structure to a five-coordinate hypervalent one. Along with these structural changes, the oxidation state of the phosphorus atom changes from +III to +V. The last step is the rate-determining step with a $\Delta G^{0\neq}$ value of 29.1 kcal/mol, which is much smaller than those of the intra-molecular isomerizations.

Next, an inter-molecular hydrogen exchange pathway was also examined, which occurs through the mutual hydrogen transfers between two **4OP** molecules via **TS$_{4OP/4PP}$**; see Figure 3. **TS$_{4OP/4PP}$** is not symmetrical, in which the O2-H2 (1.025 Å) and O2′-H2′ (1.457 Å) distances are very different. As shown in Figure 2, **4PP** is somewhat less stable than the reactants (**1P** + ammonia-borane) by 4.6 kcal/mol. When the cyclic dimerization of NH_2=BH_2 to (NH_2-BH_2)$_2$ is considered, the endothermicity decreases but the reaction is still endothermic by 2.2 kcal/mol; see the dashed line in Figure 2. These results are consistent with the experimental observation that **4PP** is converted to **1P** with the release of H_2.[17]

Summarizing the above results, **1P** reacts with ammonia-borane via the P-O cooperation pathway to afford an intermediate **4OP**. Then, **4OP** isomerizes to **4PP** either through the assistant of NH_2=BH_2 or through the inter-molecular hydrogen transfer between two **4OP** molecules.[18]

4PP was experimentally proposed to be an active species in the hydrogenation reaction of azobenzene with ammonia-borane. Considering this proposal, we investigated the reaction of **4PP** with azobenzene. When azobenzene approaches **4PP**, the H2 atom migrates from the phosphorus atom to the N3 atom through a transition state **TS$_{4PP/8}$** to form an intermediate **8**; see Figure 4. The $\Delta G^{0\neq}$ and ΔG^{0} values are 27.5 and 29.4 kcal/mol, respectively.[19] The intermediate **8** is understood to be an ion-pair between a phosphonium cation and a deprotonated diphenylhydrazine anion [PhN-NHPh]$^-$. Then, the N4 atom of the [PhN-NHPh]$^-$ is bound with the cationic phosphorus center to form a very stable intermediate **9** through a rotational transition state of the [PhN-NHPh]$^-$ moiety. Though the transition state could not be optimized, it is likely that this process easily occurs because the [PhN-NHPh]$^-$ moiety is sufficiently distant from the phosphorus center. This step is significantly exothermic by 39.8 kcal/mol. At last, the reductive elimination occurs to yield diphenylhydrazine and regenerate **1P** with a large $\Delta G^{0\neq}$ value of 43.2 kcal/mol relative to **9** which is the most stable intermediate.

Considering that the insertion of the C=O double bond of ketone into the Ge-H bond was experimentally and theoretically reported,[1b,3,20] we investigated the insertion reaction of the N=N double bond of azobenzene into the P-H bond. However, it needs a large $\Delta G^{0\neq}$ value (53.5 kcal/mol); see Figure S5 in SI. All these results indicate that **4PP** is not an active species for the hydrogenation of azobenzene.

Besides **4PP**, **4OP** is expected to be able to perform the hydrogenation of azobenzene, because the H1 and H2 atoms of **4OP** are considered to be reactive for hydrogenation reaction. This reaction occurs through a concerted transition state **TS$_{4OP/1P}$** to produce **1P** and diphenylhydrazine **10**; see Figure 4. The $\Delta G^{0\neq}$ value is 28.1 kcal/mol, which is much smaller than that of the hydrogantion reaction by **4PP** as discussed above. This $\Delta G^{0\neq}$ value is not different very much from the experimental value (23.7 kcal/mol at 313.15 K), where the experimental $\Delta H^{0\neq}$ and $\Delta S^{0\neq}$ values (12.4 ± 0.7 kcal/mol and -36 ± 7 eu, respectively)[5] were employed. Based on these results, it should be concluded that not **4PP** but **4OP** is the active species for the transfer hydrogenation reaction.

Radosevich et al. reported that **4PP** could catalyze the transfer hydrogenation but less effeciently than **1P**.[5] This fact is explained, as follows: **4PP** transforms to **4OP** via the NH_2=BH_2-assisted or the inter-molecular hydrogen transfer pathway; see Figure 3. Then, **4OP** reacts with azobenzene to regerenate **1P** with the release of **10**. After that, the catalytic hydrogenation is performed by **1P**. Besides the transformation to **4OP**, **4PP** can also react with azobenzene. This reaction leads to a very stable intermediate **9** as discussed above. Note that both the β-H abstraction and the reductive elimination are difficut to occur from **9**; see Figure 4. This means that some amount of **4PP** is trapped as **9** during the reaction. As a result, the catalytic hydrogenation by **4PP** occurs more slowly than that by **1P**.

We investigated the substituent effect on the activity of the catalyst. The substitution of CF_3 for ^{t}Bu somewaht decreases the $\Delta G^{0\neq}$ values for **TS$_{1P/4OP}$** and **TS$_{4OP/1P}$** to 20.9 kcal/mol and 23.5 kcal/mol, respectively, indicating that the electron-withdrawing group is favorable for the catalytic reaction; see Figures S6 in SI. On the other hand, the substitution of H for ^{t}Bu little changes the $\Delta G^{0\neq}$ value for **TS$_{1P/4OP}$** and moderately decreases the $\Delta G^{0\neq}$ value for **TS$_{4OP/1P}$**, indicating that the bulkyness of the substituent is not important; see Figure S7 in SI. However, the transformation of **4OP** to **4PP** is little influenced by both substitutions; see Figure S8 in SI .

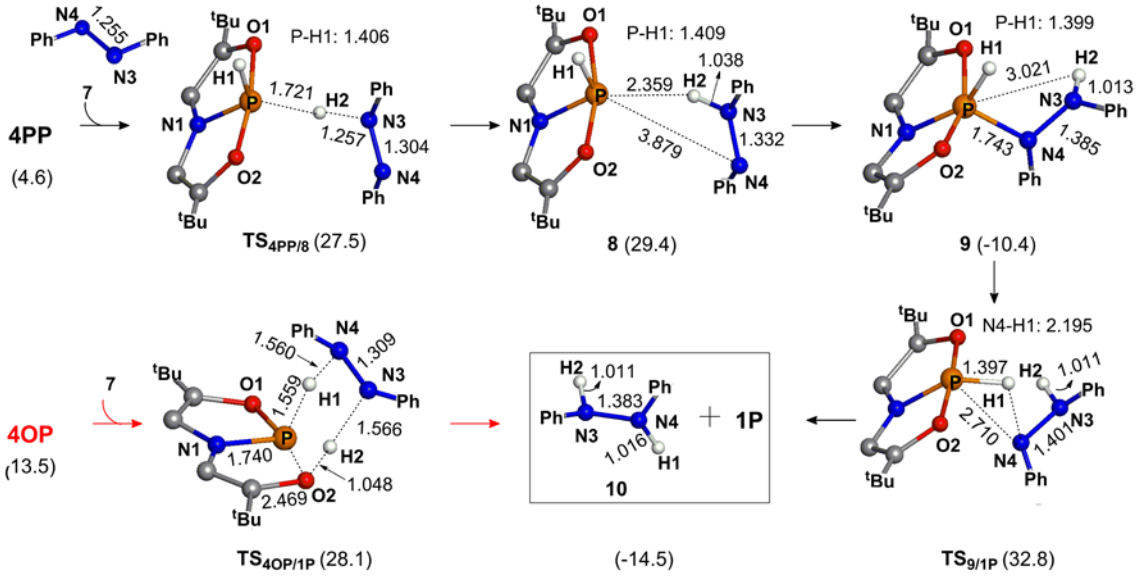
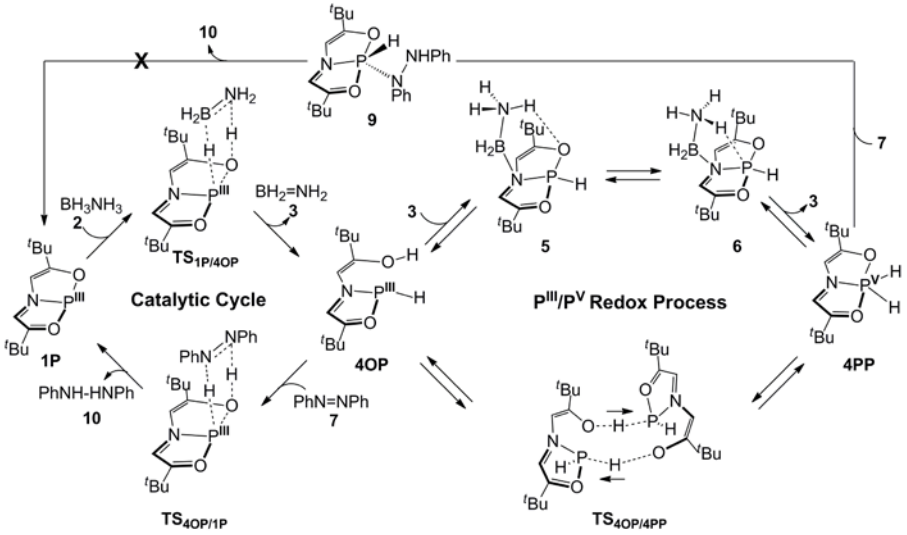


Figure 4. Geometry changes in the hydrogenation reaction of azobenzene by **4PP** and **4OP**. Distances are in Å.

In conclusion, the mechanistic details of the transfer hydrogenation reaction by a trivalent phosphorus compound **1P** were theoretically disclosed here. As summarized in Scheme 2, 1) the catalytic cycle occurs through a new concerted P-O cooperation mechanism, 2) the active species of the transfer hydrogenation is **4OP**, which is produced from **1P** through dehydroggenation of ammonia-borane, 3) this P-O cooperative reaction resembles well the metal-ligand cooperation reaction by the transition metal complex with pincer ligand, 4) the P^{III}/P^{V} redox certainly occurs in the mutal conversions between **4OP** and **4PP**, but it is not involved in the catalytic cycle, and 5) the substitution of a electron-withdrawing CF_3 group for ^{t}Bu imporves the catalytic activity of the trivalent phosphorus compund.



Scheme 2. Catalytic cycle of transfer hydrogenation by **1P** via the P-O cooperation and mutual transformation between **4OP** and **4PP** via the P^{III}/P^{V} redox processes.

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[16] The B3PW91-calculated $\Delta G^{0\neq}$ values are 32.1 and 32.9 kcal/mol for $\mathbf{TS_{6/4PP}}$ and $\mathbf{TS_{4OP/4PP}}$, respectively. Only here, the B3PW91-calculated value is presented because the ONIOM(CCSD(T):MP2) calculation is difficult to be carried out for the large size of $\mathbf{TS_{4OP/4PP}}$.

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[18] In the early stage of the reaction, the BH_2=NH_2-assisted isomerization mainly occurs, while the inter-molecular hydrogen exchange would occur when the concentration of **4OP** becomes larger.

[19] This unreasonable energy change may arise from the difference in the quality between the ONIOM and DFT methods. In DFT calculation, **8** is lower than $\mathbf{TS_{4PP/8}}$ by 2.2 kcal/mol in Gibbs energy.

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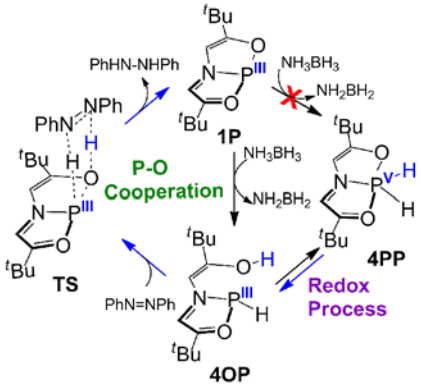
Catalytic Transfer Hydrogenation by Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P^{III}/P^{V} Redox Pathway?



The catalytic transfer hydrogenation of azobenzene with ammonia-borane by **1P** occurs via the P-O cooperation mechanism, where an active species is **4OP**. This P-O cooperation mechanism is newly found here in the main-group element compound, which resembles well the M-L cooperation by the transition-metal complex with pincer ligand. When azobenzene is absent, the P^{III}/P^{V} redox certainly occurs in the isomerization of **4OP** to **4PP** but it is not involved in the catalytic transfer hydrogenation.